Biogeochemistry of Barium and other Elements from Certain Plant Species Growing on Barite Mining Area, Andhra Pradesh, South India

L. Chandra Sekhar Reddy
Department of Geology, Loyola College, Pulivendla-516390, Kadapa District, Andhra Pradesh, India

Abstract

Plant species growing on barite mining area and their substrate samples were collected in Vemula of Kadapa district, Andhra Pradesh. Trace element analysis of these samples was carried out for Ba, Pb, Zn, Cu, Co, Ni, and Mo and the biological absorption co-efficient (BAC) was calculated for each element for the five plant species viz Calotropis gigantean, Cassia ariculata, Flacourtia indica, Gardenia latifolica, and Gymnosparia falconeria. BAC is used to characterize the intensity of absorption of chemical elements from their substrate. It is the ratio of the concentration of an element in plant ash to that of its substrate. The results reveal that in the study area certain elements are present in plants and the same elements are not detected in their soil. In contrast to this some elements are not detected in plants and the same elements are present in their soil. Based on BAC the behavior of plants under study was revealed that Ba shows strong absorption in stem and leaves of Flacourtia indica, and Cu shows strong absorption in stem of Gardenia latifolica. Furthermore Zn shows strong absorption in leaf and stem of Calotropis gigantia. These plant species may be considered as accumulator plants and may be useful in mineral exploration. These plant species may also be useful in reclamation and revegetaion of adversely affected mining environments. Further, the biogeochemical data may be considered for the monitoring of the pollution levels of mining environment.
KEYWORDS: Biogeochemistry, Trace elements, BAC, Accumulator Plants, Barite mining, Vemula.

Introduction: The plant species which have the ability to successfully germinate grow and reproduce under adversely affected environments to be useful for reclamation and revegetation. Plants are greatly influenced by the presence of excess or deficiency of mineral nutrients, and they may also be subject to toxic effects due to heavy metals. However certain plants have the unusual adaptability to withstand heavy metal toxicity, and such plants are referred to as indicator plants. Generally such indicator plants are accumulator plants which have unusual affinities for relatively rare elements, most of them heavy metals, which may or may not be essential to them. Metal hyper accumulating plants are useful in phytoremediation and play a vital role in biogeochemical prospecting, and have implications on human health through food chain[1].The important use of plant species for determining the chemical properties of the substrate on which the vegetation grown has been a great importance in the evaluation the soil quality. The composition of plant tissues reflects the composition of the soil in which the plant grows. This interrelationship however is modified in many plants by tolerance mechanisms. Thus, plants are able to accumulate most chemical elements and many species are sensitive indicators of the chemical environment in which they grow, and also the element content at different of the same plants may be widely divergent [2,3,4.] Trace elements play an important role in biological activities and therefore, deficiency or excess in human beings can lead a number of disorders [5]. In recent years the role of trace elements studies in environmental geochemistry is giving attention.

Bjiogeochemical exploration involving soil-plant relationship and consists of chemical analysis of plants to get tangible proof of mineralization in the substrate. Chemical analysis of systematically sampled trees and shrubs for traces of ore metals was one of the first geochemical methods to be investigated[6].Biogeochemical province[7] is influenced by local enrichment of metals due to the existence of ore bodies and their associated dispersion halos. In such provinces plants conspicuously exhibit indicator characteristics which may be morphological or physiological. Biogiochemistry is applicable in regional geochemical reconnaissance applied to agriculture[8] and in applied to environmental geochemistry to tackle various problems of practical importance[9]. Although biogeochemical studies have established a number of accumulator plants for several elements, barium accumulators are rather hard to find in the literature. Barium is a moderately toxic element to the plants[10]. The aim of the present study is to characterize some of the plant species that naturally colonized in and around barite mine and to determine the metal accumulation pattern in the sampled plant species for the Ba and other associated elements. The objective is to asses these plants for their ability to uptake and accumulates the Ba in different organs of the plants.

Study Area: Barite is a naturally occurring barium sulphate mineral. A significant portion of the total known reserves in the world is found in Andhra Pradesh. The barite deposit of Vemula region (Lat. 14^{o} 19’ 00” - 14^{o} 21’ 00” N: Long 78^{o} 22’ 30” E) of Cuddapah District, Andhra Pradesh is included in the Survey of India toposheet No 57 J/7. The study area is about 65 Km from the district headquarter Kadapa and 15 Km from Pulivendla the mandal headquarter. In this area the basaltic hills generally flat-topped and are bald at some places. A chain of hills trending E-W with a relief varying from few meters to 550m. Vemula barite deposit associated with basic intrusives occurs within the Vempalli stage of the Lower Cuddapah in the Southern part of the Cuddapah basin[11] .The Vempalli formation is intruded, along the bedding planes, by sills of doleritic and basaltic composition marking an important period of igneous activity in Peninsular India [12]. Barite occurs as veins, stringers and fissure fillings along the planes of fracture, fault planes and joints mainly in the traps. This area primarily consists of conglomerates, shales, basalts, dolomites and dolomitic limestones. Earlier workers have carried out in mineralogical[13] petrogenetical[12], biogeochemical[14,15,16] and hydrogeochemical [17] aspects.

Sampling and Analytical Methods: After a preliminary geobotanical survey of the area five plant species viz., *Calotropis gigantean, Cassia ariculata, Flacourtia indica, Gardenia latifolica, and Gymnosparia falconeria* were selected for biogeochemical investigations. Systematic sampling of plants and soils was carried out. Composite samples of leaves and stem of these plant species along with their substrate were collected. Samples of surface soils were collected from pits measuring 15X15X15 cm. Similarly, six to eight spot samples of surface soils were collected surrounding the plants and combined to form a composite sample. Care was taken to collect mature and healthy plant organs. All the plant samples were washed thoroughly with distilled water.

Moisture from these samples was eliminated by keeping them at 110^o C in a hot air oven for eight hours. Further these samples were ignited and ashed at 450^o C in a muffle furnace. The plants ashes have been digested in 2M HCl. Samples of soils were oven dried at 110^o C in a hot air oven for eight hours. These soils were disintegrated in a porcelain mortar and were sieved to pass through 2 mm sieve mesh. From these samples organic matter was expelled by placing them in a muffle furnace at 450^o C for eight hours and digested in aquaregia [18]. The plant and soil samples were analyzed for various trace elements viz., Ba, Pb, Zn, Cu, Co, Ni, and Mo by AAS [4] and the values of the elemental data are given in Table 1and 2.

Table 1. **Trace elements (ppm) in plants and soils of the study area Vemula**

Element	Gardenia latifolica					Flacourtia indica					Calotropis gigantean				
	Soil	Leaf (L)	L-BAC	Stem (S)	S-BAC	Soil	Leaf (L)	L-BAC	Stem (S)	S-BAC	Soil	Leaf (L)	L-BAC	Stem (S)	S-BAC
Ba	590	ND	0	ND	0	600	6096	10.16	7650	12.75	915	815	0.89	348	0.38
Pb	37	78	2.1	36	0.97	38	28	0.73	39	1.02	46	19	0.41	14	0.3
Zn	80	139	1.73	142	1.77	120	17	0.14	131	1.09	80	832	10.4	1292	16.15
Cu	32	40	1.25	269	8.4	27	20	0.74	7	0.26	16	32	2	14	0.87
Co	28	31	1.10	3	0.1	40	38	0.95	4	0.1	48	33	0.68	14	0.29
Ni	21	15	0.71	26	1.23	18	ND	0	ND	0	15	ND	0	ND	0
Mo	ND	7	-	5	-	ND	10	-	15	-	ND	2.5	-	3	-

ND = Not detected; BAC= Biological Absorption Co-efficient

Table 2. **Trace elements (ppm) in plants and soils of the study area Vemula**

Element	Soil	Cassia Ariculata		Gymnosparia falconeria	
		Leaf (L)	L-BAC	Leaf (L)	L-BAC
Ba	945	123	0.13	ND	0
Pb	15	10	0.66	33	2.2
Zn	60	100	1.66	43	0.7
Cu	15	12	0.80	12	0.80
Co	24	ND	0	ND	0
Ni	15	ND	0	ND	0
Mo	ND	15	-	19	-

ND = Not detected; BAC= Biological Absorption Co-efficient

Results and Discussions: From the analytical data (Table 1 and 2) it may be seen that generally certain elements are present in plants and the same elements are not detected in their soil. In contrast to this some elements are not detected in plants and the same elements are present in their soil. Ba in *Gardenia latifolica, and Gymnosparia falconeria*; Ni in *Cassia Ariculata, Flacourtia indica, Calotropis gigantea* and *Gymnosparia falconeria*; Co in *Cassia Ariculata and Gymnosparia falconeria* plant species is not detected but these elements are present in their substrates (Table 1 and 2). In contrast to this Mo is not detected in soils, but this element is present in all plants. (Table 1 and 2) This may be attributed due to biogeochemical cycling of elements involving differential migration in vertical as well as lateral directions through the soil profile shows the absence of an element in the surface soil [14]. The presence of an element in soil and absence of the same element in plants is due to exclusion mechanism and/or bioavailability of the element[10,4,19,6]. And this also may be attributed due to absorption mechanisms by plant roots vary for different ions. Hence due to biogeochemical cycling of elements a wide variety of elemental responses in plant-soil relations are exhibited.

Trace elemental concentration in plants and soils: The concentrations of Pb, Zn, Cu, Co, Ni, and Mo in *Gardenia latifolica* ; Ba, Pb, Zn and Mo in *Flacourtia indica*; Cu, Mo and Zn in *Calotropis gigantean*; Mo and Zn in *Cassia Ariculata*; Pb and Mo in *Gymnosparia falconeria* are high than their substrates, and the converse is true for Ba in *Gardenia latifolica*; Cu, Co and Ni in *Flacourtia indica*; Ba, Pb, Co and Ni in *Calotropis gigantean*; Ba, Pb, Cu, Co and Ni in *Cassia Ariculata*; and Ba, Zn, Co, Ni and Cu in *Gymnosparia falconeria*. Furthermore Pb, Co was highly accumulated in the leaves of *Gardenia latifolica* than in stem; Cu and Co was high in the leaves of *Flacourtia indica* than in its stem. Similarly Ba, Pb, Cu, and Co was more highly accumulated in the leaves of *Calotropis gigantean* than in stem.

Cu, Ni was high in the stem of *Gardenia latifolica* than in leaves; Ba, Pb, Zn, and Mo are more highly accumulated in the stem of *Flacourtia indica* than in leaves; similarly the elemental concentration of Zn was high in the stem of *Calotropis gigantean* than in leaves. The different organs of plant species exhibit different behavior with reference to elemental concentrations and their mobile nature and each plant species has a different requirement for, and tolerance to trace elements[20]. Tiagi[21] stated that different plant organs show wide variations in respect of accumulation of different elements.

Based on the observations among the selected the five vegetation/plant species (both leaves and stem) except *Flacourtia indica* the others show lower concentrations of barium range of ND (Not Detected) to 815 ppm though their substrate contains appreciable amount of barium (590-945 ppm). Conspicuously *Flacourtia indica* exhibits unusual accumulation of barium with a concentration of 6096 ppm in leaves and 7650 ppm in stem while its substrate contains only 600 ppm of barium. From this it is concluded that *Flacourtia indica* has been identified as an accumulator plant of barium.
Gardenia latifolica exhibits maximum accumulation of copper with a concentration of 269 ppm in the stem while its substrate contains only 32 ppm. *Calotropis gigantean* contains appreciable amount of Zn (1292 ppm) in their stem while its substrate contains 80 ppm only. Earlier in Vemula area the shoot of *Indigofera cordifolia* for Ba, root of *Cassia angustifolia* for Sr, and the leaves of *Kirganelia reticulate* for Co considered as accumulator plants [14].

Biological Absorption Co-efficient (BAC): Biological Absorption Coefficient [22] is used to characterize the intensity of absorption of chemical elements from their substrate. BAC values were calculated for each element for the five plant species (Table 1 and 2). Based on BAC the behavior of plants under study was revealed as Ba shows strong absorption in stem and leaves of *Flacourtia indica*, and Cu shows strong absorption only in stem of *Gardenia latifolica*. Furthermore Zn shows strong absorption in leaf and stem of *Calotropis gigantean*. The other elements are not of any utility as these are having low absorption and/or intermediate absorption.

In the study area it was observed that the BAC values of the both stem (12.75) and leaf (10.16) of *Flacourtia indica* for Ba is found to be significantly high, whereas the BAC of this element ranges from 0 to 0.89 in the remaining plant species. Therefore *Flacourtia indica* may be considered as accumulator plant for barium. The Ba concentration in the *Flacourtia indica* species is generally higher than the other plant species growing on the study area of barite mining. Dunn and Hoffman[23] noticed that in certain plans like birch, jack-pine, black spruce, Labrador tea, alder and willow in Saskatchewan are capable of absorbing large amounts of Ba (12000 ppm).[24] (1971) have also noticed the Ba uptake was greater in bush beans. Earlier Raghu[14] have noticed that *Indigofera cordifolia* for Ba considered as accumulator plants without taking into account their substrate concentration considered as accumulator plant in this study area. Similarly it was observed the BAC values for the root of *Gardenia latifolica* for Cu (BAC 8.4) and stem and leafs of *Calotropis gigantean* for Zn (BAC (stem) 16.15; BAC (leaf) 10.4) is found to be significantly high. Therefore *Gardenia latifolica* may be considered as an accumulator plant for Cu and *Calotropis gigantean* for Zn may be considered as an accumulator plant. Earlier Raghu[14] have noticed the *Tephrosia purpurea* for Zn considered as accumulator plant based on BAC. This study has given greater scope on the plant-soil relationship in the mining/mineralized areas and their significance in biogeochemical orientation surveys, environmental studies and in mineral exploration. These plant species can also be used in reclamation and revegetation of the adversely affected areas. Further it needs detailed biogeochemical investigations are required to establish these plant species are as an indicator for exploration of barium deposit.

Conclusions: In the study area, the results revealed that certain elements are present in plants and the same elements are not detected in their soil. While some elements are not detected plants and the same elements are present in their soil. Due to biogeochemical cycling of elements, a wide variety of elemental responses in plant-soil relation are exhibited. Based on the observations among the selected the five plant species except *Flacourtia indica* the other plants show lower concentrations of barium though their substrate contains appreciable amount of barium. Conspicuously *Flacourtia indica* exhibits unusual accumulation of barium with a concentration of 6096 ppm in leaves and 7650 ppm in stem, while its substrate contains only 600 ppm of barium. Hence *Flacourtia indica* may be considered as accumulator plant for Ba. Similarly gardenia latifolica exhibits maximum accumulation of copper with a concentration of 269 ppm in the stem while its substrate contains only 32 ppm. Hence *Gardenia latifolica* may be considered as accumulator plant for Cu. *Calotropis gigantean* contains appreciable amount of Zn (1292 ppm) in their stem while its substrate contains 80 ppm only. Therefore *Calotropis gigantean* may be considered as accumulator plant for Zn. Based on BAC the behavior of plants under study was revealed that Ba shows strong absorption in stem and leaves of *Flacourtia indica*, and Cu shows strong absorption in stem of

Gardenia latifolica. Furthermore Zn shows strong absorption in leaf and stem of *Calotropis gigantia*. The plant species *Flacourtia indica*, *Gardenia latifolica*, and *Calotropis gigantia* may be considered as accumulator plants for Ba, Cu and Zn respectively and these plants may also be useful in mineral exploration. However, detailed biogeochemical investigation is required further to get clear picture of accumulator plants. These plant species may also be useful in reclamation and revegetaion of adversely affected mining environments. Further, the biogeochemical data may be considered for the monitoring of the pollution levels of mining environment. This study has given greater scope on the plant-soil relationship in the mining/mineralized areas and their significance in biogeochemical orientation surveys and environmental studies

Acknowledgements: I deem it a great privilege to express my deep sense of gratitude to my research supervisor, the Late prof. E.A.V. Prasad, but for whose guidance this paper could not have come up to its present form. I gratefully acknowledge the help of Dr. V. Raghu, Dr. G. Sankaranna, Dr. M. Jayarama Gupta and Prof. A. Nagaraju, department of Geology S.V.University Tirupati for their kind help in various ways during this study.

References

1. Kabata Pendias, A. (2001). Trace elements in soils and plants. Third Edition. CRC press, Inc.
Boca Raton, Florida, 432p.
2. Kovaleveskii, A.L. (1987).Biogeochemical Exploration for Mineral deposits. VNU Science Press, Netherlands, pp.224.
3. Erdman, J.A. (1990). Biogeochemical baselines and the importance of the species, plant parts, and the season- the U.S. Geological Survey's studies of big sage brush in the West. In: B.R. Doe (ed). Proceedings of U.S. Geol. Survey workshop on Environmental geochemistry. U.S. Geol. Survey circular. v. 1033, pp.45-46.
4. Brooks R.R., Dunn C.E. and Hall G.E.M., (Eds). (1995). Biological systems in mineral Exploration and processing Ellis Horwood Limited, Hemel Hempstead, U.K. 538p.
5. Underwood, E. J. (1971). Trace elements in human and animal nutrition, 3rd edn. Academic Press, New York, 479p.
6. Rose A.W., Hawkes H.E. and Webb J.S.(1979). Geochemistry in Mineral Exploration. 2nd edn. Academic Press, London, 657p.
7. Vinogradov, A.P. (1964). Biogeochemical provinces and their role in organic evolution (in French). Int. Monograph Earth Sci., v.55, pp. 317-337.
8 Joyce, A.S.(1975). Application of regional geochemical reconnaissance to agriculture. In : Trace Elements in soil-plant-animal systems (eds : d. J.D. Nicholas and A.R. Egan) , Academic Press, Inc . New york , pp.325-328.
9. Thornton I. (1983). Geochemistry applied to agriculture. In:Thornton, I (Ed) Applied Environmental Geochemistry, Academic Press, London, pp.231-266.
10. Brooks, R.R. (1972). Geobotany and biogeochemistry in mineral exploration. Harper and Row, New york, 290p.
11. Prasad R.N. and Prasannan E.B. (1976) Asbestos-barytes-steatite mineralization in the lower Cuddapah of Andhra Pradesh,. Geol. Survey.India, Misc. Publ, v.23,pp.560-568.

12. Gangadhar, V., Ramana Rao, N. and Sudhakara Reddy, Y. (1983). The petrography of basalts from Vemula area, Pulivendla taluk, Cuddapah District. Jour. Ind. Acad. Geo. Sci., v. 26, pp.52-61
13. Krishnan, M.S. (1953). Asbestos and barites in Pulivendula taluk, Cuddapah District. Bull. Geol. Surv. India., v.5, pp.1-53.
14. Raghu, V. (2001). Accumulation of elements in plants and soils in and around Mangampeta and Vemula barite mining areas, Cuddapah district, Andhra Pradesh. India. Env. Geology, v.40, pp.1265-1277.
15. Raghu, V. (2007). Termite mounds as bioindicator for the exploration of barite in the area around vemula mine, Kadapa District, Andhra Pradesh. Ind. Jour. Geochemistry, v.22(1), pp.45-46.
16. Reddy L. Chandrasekhar., Reddy K.V. Ramana. and Humane Sumedh, K. (2012). Distribution of trace elements in coconut water and mine water from barite mineralized zone, Cuddapah District, Andhra Pradesh, India. Int. Res. Jour. Env. Sci., v. 1(5), pp.22-26.
17. Chandrasekhar Reddy, L., Deshpande, S.M., Ramana Reddy, K.V. and Aher, K.R. (2012). Hydrogeochemical processes in the groundwater environment of Vemula area, Kadapa District, South India. Int. Jour. Recent Trends in Sc. Tech., v.3(1), pp.18-24.
18. Brooks, R.R. (1983). Biological methods of prospecting for minerals. John Wiley and Sons, New York, 322p.
19. Kovaleveskii A.L.(1979). Biogeochemical exploration for mineral deposits Amerind Publ Co. Pvt Ltd, New Delhi, 136p.S
20. Dunn, C.E., Brooks, R.R., Edmondson, J., Leblance, M. and Reeves, D. (1996). Biogeochemical studies of metal-tolerant plants from Southern Marocco. Jour. Geochem. Expl., v. 56, pp. 3-22.
21. Tiagi, Y.D. (1990). Geobotany and biogeochemistry in mineral prospecting. Presendential address, Botany section, Proc 77th Indian Sci. Congr., Cochin, pp.1-26.
22. Kovaleveskii, A.L. (1969). Some observations in biogeochemical parameters (in Russian). Trudy Buryat Inst Estestvenn Nauk. v.2, pp.195-214.
23. Dunn C.E. and Hoffman, E. (1986). Multi-element study of vegetation from a Zone of rare-earth rich allanite and apatite in northern Saskatchewan, Canada. Appl.Geochem, v.1, pp.375-381.
24. Wallace, A. and Romney, E.M. (1971). Interactions of calcium, strontium and barium in plants. Agron. Jour, v.63, pp.245-248.